

赧桐的化学成分

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摘要 应用正反相硅胶柱层析、中压柱层析、制备性薄层层析等手段, 从赧桐(*Clerodendrum japonicum*)中分离得到 4 个苯丙素甙类成分, 根据光谱数据及化学方法, 鉴定为马蒂罗甙(1), 单乙酰马蒂罗甙(2), 贞桐甙 A(4)以及阿克甙(3), 其中, 贞桐甙 A 是一新化合物。同时还得到 22,23-二氢菠甾醇、豆甾醇、25,26-去氢豆甾醇, 乌索酸, 丁二酸酐和小麦黄素等。

关键词 赧桐, 马鞭草科, 苯丙素甙, 贞桐甙 A

CHEMICAL CONSTITUENTS FROM CLERODENDRUM JAPONICUM

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Abstract By means of silica gel and reversed phase silica gel CC, medium pressure CC, as well as preparative TLC, four phenylpropanoid glycosides were isolated from *C. japonicum*. According to spectral data and chemical methods, they were determined as martinoside (1), monoacetyl martinoside (2), acteoside (3) and clerodenoside A (4). Among them, clerodenoside A was a new compound, which was identified as $[\beta-(3'-\text{hydroxy}-4'-\text{methoxyphenyl})\text{-ethyl}]-2'',3''\text{-di-O-acetyl-3-O-}\alpha\text{-L-rhamnopyranosyl}-(4\text{-O-feruloyl})\text{-}\beta\text{-D-glucopyranoside}$ (4). In addition, 22,23-dihydrospinaesterol, stigmasterol, 25,26-dehydrostigmasterol, ursolic acid, succinic anhydride and tricin were obtained.

Key words *Clerodendrum japonicum*; Verbenaceae; Phenylpropanoid glycosides; Clerodenoside A

INTRODUCTION

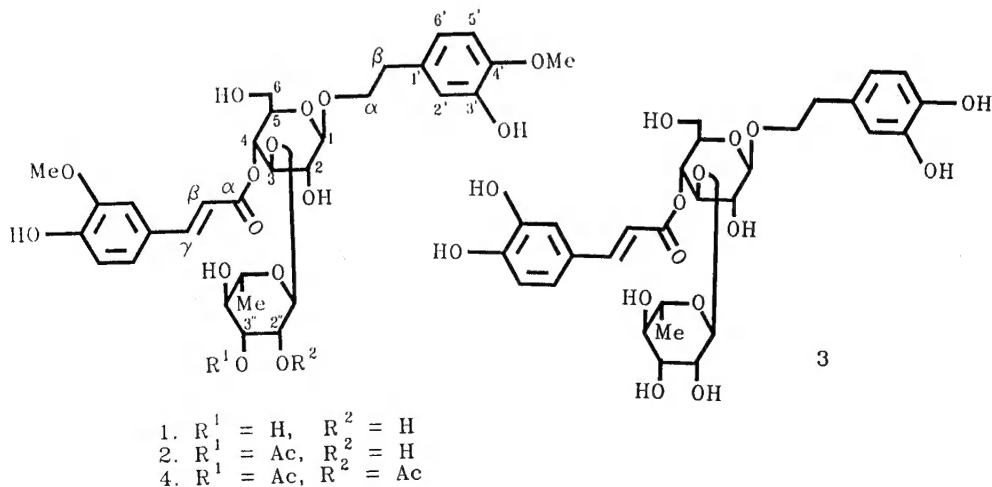
The genus *Clerodendrum* (Verbenaceae) with more than 400 species is widely distributed in the tropical and subtropical regions^[1]. In China, there are about 30 species, and most of them have distribution in Yunnan province. *C. japonicum* (Thunb.) Sweet, which grows abundantly in southern China, has long been used to treat inflammation, rheumatism and malaria, as well as some woman diseases^[2]. However, its chemical constituents have not been reported so far.

RESULTS AND DISCUSSION

An alcoholic extract of the whole plant was separated into several fractions. After repeated column chromatography on silica gel and reversed silica gel, four glycosides were isolated from the EtOAc fraction. On mineral acid hydrolysis, all of them gave common sugars, D-glucose and L-rhamnose, in a ratio of 1:1. A comparison of UV, ^{13}C NMR and MS spectral data of these four glycosides with those of reported compounds showed that three of them were martiniside(1)^[3], monoacetyl martiniside(2)^[4] and acteoside(3)^[5], compound 4 was a new phenylpropanoid glycoside and named as clerodenoside A.

Clerodenoside A(4) was hydrolysed with 1mol / l KOH to afford ferulic acid. The molecular formula ($\text{C}_{35}\text{H}_{44}\text{O}_{17}$) was concluded from the peak at m/z 759 $[\text{M}+\text{Na}]^+$ and 736 $[\text{M}]^+$ in the positive FAB mass spectrum. Its fragment ion peaks were exhibited at m/z 569 $[\text{M}-\text{C}_9\text{H}_{11}\text{O}_3]^+$, 506 $[\text{M}-\text{rha}-2\text{Ac}]^+$, 339 $[\text{506}-\text{C}_9\text{H}_{11}\text{O}_3]^+$ and 231 $[\text{rha}+2\text{Ac}]^+$, indicating that the two Ac groups were connected with the terminal rhamnose, and this was supported by comparing with martiniside(1). Compound 4 had one more Ac group than monoacetyl martiniside(2) in the ^1H and ^{13}C NMR spectra, and this additional Ac group was proved to be located at C-2 of rhamnose, because the C-2 of rhamnose was displaced downfield at δ 71.4, whereas C-1 and C-3 were shifted upfield at 100.3 and 73.2, respectively (Table 2). Thus, the structure of 4 was elucidated to be $[\beta-(3'-\text{hydroxy}-4'-\text{methoxyphenyl})\text{-ethyl}-(2'',3''\text{-di-O-acetyl-3-O-}\alpha\text{-L-rhamnopyransyl})-(4\text{-O-feruloyl})-\beta\text{-D-glucopyranoside}]$.

In addition, from the pet.-ether and n-BuOH fractions, we obtained 22,23-dihydrospinaesterol, stigmasterol, 25,26-dehydrostigmasterol, ursolic acid, succinic anhydride and tricin. Interestingly, in the genus *Clerodendrum*, clerodane-type diterpenoids are the characteristic chemical constituents, while no diterpenoid but some phenylpropanoid glycosides have been mainly isolated from *C. japonicum*. Such difference may be of chemotaxonomical significance.



EXPERIMENTAL SECTION

Mps. uncorr. ^1H and ^{13}C NMR were recorded on Bruker AM-400 with TMS as int. standard. Optical

rotations were measured in Horiba Sepa-300.

Plant material *Clerodendrum japonicum*(Thunb.) Sweet was collected in Xishuangbanna of Yunnan province, China. A voucher has been deposited in the Herbarium of Kunming Institute of Botany.

Extraction and isolation The dried and powdered herbs(5400g) were extracted with 95% EtOH under reflux. After the removal of solvent by evapn., the residue(362g) was suspended in H₂O and then successively fractionated with pet.-ether(60–90°C), EtOAc and n-BuOH. The EtOAc extract (72g) was subjected to CC over silica gel eluting with CHCl₃–Me₂CO (from 10:1 to 2:1) to give frs. A–F. Fr.B (3.5g) was chromatographed on medium pressure column developing with CHCl₃–Me₂CO (8:1) to afford compound **4**(270mg). Fr.C (1.3g) was purified by a column on Lobar RP-8 with 30% MeOH to yield compound **2**(85mg). Fr.E (18g) was subjected to CC on silica gel with CHCl₃–MeOH–H₂O (from 50:10:1 to 20:10:1) to provide compounds **1**(2.5g) and **3**(1.2g).

Table 1 ¹H NMR spectral data of compounds 1–4(in CD₃OD, TMS internal standard, 400 MHz)

	1	2	3	4
Aglycone				
2	6.73d(2)	6.73d(2)	6.68d(2)	6.72d(2)
5	6.80d(8)	6.80d(8)	6.67d(8)	6.80d(8)
6	6.68dd(8,2)	6.68dd(8,2)	6.55dd(8,2)	6.68dd(8,2)
α	2.82dt(7,2)	2.82dt(8,2)	2.78dt(8,2)	2.82dt(8,2)
β	3.72dd(11,8)	3.72dd(11,8)	3.71dd(12,8)	3.70dt(11,8)
	4.05dd(8,7)	4.04dd(8,7)	4.02dd(8,6)	4.03dd(8,6)
OMe	3.80 3H,s	3.81 3H,s		3.81 3H,s
Acyl moiety				
2	7.19d(2)	7.19d(2)	7.05d(2)	7.19d(2)
5	6.81d(8)	6.81d(8)	6.76d(8)	6.81d(8)
6	7.07dd(8,2)	7.08dd(8,2)	6.94dd(8,2)	7.08dd(8,2)
β	6.37d(16)	6.38d(16)	6.26d(16)	6.38d(16)
γ	7.65d(16)	7.66d(16)	7.58d(16)	7.67d(16)
OMe	3.88 3H,s	3.88 3H,s		3.88 3H,s
glucose				
1	4.37d(8)	4.37d(8)	4.36d(8)	4.35d(8)
Rhamnose				
1	5.19d(1.6)	5.17d(1.6)	5.18d(1.6)	5.18d(1.6)
6	1.09 3H,d(6)	1.11 3H,d(6)	1.08 3H,d(6)	1.12 3H,d(6)
2-OAc				2.05 3H, s
3-OAc		2.07 3H,s		1.96 3H, s

Compound 1 amorphous white powder, $[\alpha]_D^{14}$ –85.48°(c 0.027, MeOH); $UV\lambda_{max}^{EtOH}$ nm(log ϵ): 219.5(4.35), 229(sh, 4.12), 285.5(4.02), 298.5(sh, 4.00), 328(4.18); $IR\nu_{max}^{KBr}$ cm^{–1}: 3400(OH), 2920, 1700, 1620, 1590, 1510(Ar), 1425, 1270, 1160, 1030, 810; ¹H NMR and ¹³C NMR data see Table 1 and Table 2.

Compound 2 amorphous white powder, $[\alpha]_D^{14}$ –68.10°(c 0.026, MeOH); $UV\lambda_{max}^{EtOH}$ nm(log ϵ): 218(4.32), 231(4.22), 246(sh, 4.03), 287(4.10), 302(sh, 4.08), 328(4.31); $IR\nu_{max}^{KBr}$ cm^{–1}: 3400(br, OH), 1700, 1625, 1590, 1510(Ar), 1260, 1150, 1030; ¹H NMR and ¹³C NMR data see Table 1 and Table 2.

Compound 3 amorphous white powder, $[\alpha]_D^{14}$ –85.51°(c 0.052, MeOH); $UV\lambda_{max}^{EtOH}$ nm(log ϵ): 220(4.22), 247(3.92), 292(4.00), 304(sh, 4.04), 335(4.17); $IR\nu_{max}^{KBr}$ cm^{–1}: 3400(br, OH), 2920, 1690, 1600, 1515(Ar), 140,

1280, 1160, 1040, 810; ^1H NMR and ^{13}C NMR data see Table 1 and Table 2.

Compound 4 amorphous white powder, $[\alpha]_D^{14}$ -55.79° (c 0.027, MeOH); $\text{UV}\lambda_{\text{max}}^{\text{EtOH}}$ nm(log ϵ): 219(4.13), 230(3.94), 287.5(4.01), 293(4.08), 331.5(4.19); $\text{IR}\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3420(br, OH), 2920, 1720, 1620, 1585, 1510(Ar), 1370, 1260, 1150, 1030, 810; FAB-MS(pos.) m/z : 759([M+Na] $^+$), 736([M] $^+$), 569, 506, 339, 231(base peak); ^1H NMR and ^{13}C NMR data see Table 1 and Table 2.

Table 2 ^{13}C NMR spectral data of compounds 1—4 (in CD_3ODTMS internal standard, 400MHz)

	1	2	3	4
Aglycone				
1	133.0	132.9	131.6	133.0
2	113.0	112.9	116.4	113.0
3	147.6	147.5	144.6	147.5
4	147.5	147.1	146.1	147.4
5	117.1	117.1	117.1	117.1
6	121.2	121.2	121.3	121.2
α	72.1	72.1	72.2	72.1
β	36.6	36.5	36.5	36.5
OMe	56.5	56.4		56.5
Acyl moiety				
1	127.7	127.6	127.7	127.7
2	112.0	111.8	115.3	112.0
3	149.4	149.4	146.8	149.4
4	150.8	150.8	149.7	150.8
5	116.6	116.5	116.6	116.5
6	124.3	124.3	123.2	124.3
α	168.3	168.2	168.3	168.2
β	115.2	115.1	115.2	115.2
γ	147.9	147.9	148.0	148.0
OMe	56.5	56.4		56.5
Glucose				
1	104.3	104.2	104.2	104.2
2	76.2	76.1	76.0	76.0
3	81.5	82.1	81.6	82.0
4	70.4	70.5	70.7	70.5
5	76.1	76.0	76.2	76.0
6	62.4	62.4	62.4	62.4
Rhamnose				
1	103.0	103.0	103.0	100.3
2	72.1		70.1	72.2
3	71.4	72.4	75.6	72.4
4	73.2	73.8	71.0	73.8
5	71.2	70.8	70.7	70.7
6	70.6	18.4	18.5	18.4
2-OAc				172.2
				20.8
3-OAc	172.6			171.7
	21.1			20.7

Saponification of 4 compound 4 (80 mg) was hydrolysed with 1 mol/l KOH (50% MeOH) under reflux for 1 hr. The reaction mixture was neutralized with 36% HOAc and then concd. to dryness. The residue was partitioned between CHCl_3 and H_2O . The CHCl_3 extract was concd. to dryness and then

recrystallized with Me_2CO to give feruloyl acid. Its mp, IR and ^1H NMR data was very consistent with those reported. ^[6]

22,23-Dihydrospinaesterol Colorless needles, mp 153–155°C, $[\alpha]_D^{25} + 4.6^\circ$ (c 0.3, CHCl_3); $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3450, 2960, 2860, 1642, 1465, 1380, 1100, 1050; $\text{MS}(\text{m/z})$: 414(M^+), 399, 314, 271, 255; ^1H NMR(CDCl_3) δ : 0.54, 0.80(each 3H, s), 0.82, 0.93, 0.97(each 3H, d, $J = 7\text{Hz}$), 3.59(1H, m), 5.16(1H, dd, $J = 5, 2\text{Hz}$); ^{13}C NMR(CDCl_3) δ : 11.85, 11.20, 13.02, 18.93, 19.08, 19.80, 21.59, 22.99, 23.15, 26.36, 27.96, 29.30, 29.69, 31.52, 33.98, 34.25, 36.60, 37.20, 38.04, 39.63, 40.33, 43.43, 45.94, 49.54, 55.09, 56.16, 71.09, 117.45, 139.64. ^[7]

Stigmasterol colorless plate crystals, mp 170–172°C, $[\alpha]_D^{25} - 51.5^\circ$ (c 0.42 CHCl_3); $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3350, 2930, 1450, 1370, 1050; $\text{MS}(\text{m/z})$: 412(M^+), 397, 312, 269, 253; ^1H NMR(CDCl_3) δ : 0.65, 0.96(each 3H, s), 0.84(3H, t, $J = 7\text{Hz}$), 0.82, 0.90, 0.98(each 3H, d, $J = 7\text{Hz}$), 3.50(1H, m), 5.33(1H, d, $J = 4.8\text{Hz}$), 5.02, 5.12(each 1H, dd, $J = 14, 7\text{Hz}$); ^{13}C NMR(CDCl_3) δ : 11.68, 12.00, 18.81, 19.09, 19.40, 19.81, 21.13, 23.16, 24.33, 26.28, 28.25, 29.31, 31.73, 31.96, 34.04, 36.16, 36.56, 37.32, 39.85, 42.37, 45.96, 50.25, 56.17, 56.84, 71.83, 121.71, 129.39, 138.29, 140.83. ^[8]

25,26-Dehydrostigmasterol colorless plate crystals, mp 140–142°C, $[\alpha]_D^{13} - 36.65^\circ$ (c 0.014 CHCl_3); $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3410, 3060, 1775, 1640, 1370, 1330, 1310, 1190, 1060, 960, 890; ^1H NMR(CDCl_3) δ : 0.67(3H, s), 0.81(3H, t, $J = 7.4\text{Hz}$), 1.01(3H, d, $J = 7.8\text{Hz}$), 1.00(3H, s), 1.62(3H, s), 3.50(1H, m), 4.24(2H, m), 5.18(2H, m), 5.33(1H, d, $J = 2.0\text{Hz}$); ^{13}C NMR(CDCl_3) δ : 12.04, 12.12, 19.36, 20.21, 20.76, 21.05, 24.30, 25.69, 25.70, 28.69, 31.62, 31.87, 31.87, 36.49, 37.24, 39.66, 40.17, 42.26, 50.13, 51.96, 55.86, 56.62, 71.32, 109.50, 121.67, 130.02, 137.19, 140.74, 148.60. ^[9]

Ursolic acid: colorless needles (MeOH), mp 292–293°C(dec.), $[\alpha]_D^{19} + 59.5^\circ$ (c 0.50 CHCl_3); $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3420, 2930, 2850, 1693, 1454, 1382, 1270, 1028; $\text{MS}(\text{m/z})$: 456(M^+), 441, 426, 248(100%), 207, 203, 189, 133; ^1H NMR(CDCl_3) δ : 1.02, 1.07, 1.10, 1.23, 1.25(each 3H, s), 0.95, 0.98(each 3H, d, $J = 7\text{Hz}$), 2.63(1H, d, $J = 10\text{Hz}$), 3.45(1H, t, $J = 8\text{Hz}$), 5.46(1H, t, $J = 3.5\text{Hz}$). This compound was identified by direct comparison (mixed mp determination, TLC behavior, IR, NMR spectra) with authentic sample ^[10].

Succinic anhydride colorless needles (MeOH), mp 183–185°C, $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 2930, 1725, 1690, 1415, 1310, 1200, 1175; $\text{MS}(\text{m/z})$: 100(M^+ , 100%), 56, 28; ^1H NMR($\text{C}_5\text{D}_5\text{N}$) δ : 3.00(CH_2 , s); ^{13}C NMR($\text{C}_5\text{D}_5\text{N}$) δ : 30.40(CH_2), 175.53($\text{C}=\text{O}$).

Tricin yellow needles (MeOH), mp 296–297°C, UV $\lambda_{\text{max}}^{\text{MeOH}} \text{nm}(\log \epsilon)$: 270(4.09), 348(4.29); $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3430, 1655, 1623, 1610, 1585, 1265, 1160, 1115, 1050; $\text{MS}(\text{m/z})$: 330(M^+ , 100%), 302, 259, 213, 178; ^1H NMR($\text{DMSO}-d_6$) δ : 3.88(6H, s, $-\text{OCH}_3 \times 2$), 6.21(1H, d, $J = 2\text{Hz}$, H-6), 6.56(1H, d, $J = 2\text{Hz}$, H-8), 6.98(1H, s, H-3), 7.33(2H, s, H-2', 6'), 12.96(1H, s, 5-OH) ^[11].

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裂叶翼首花的化学成分

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CHEMICAL CONSTITUENTS FROM PTEROCEPHALUS BRETSCHNEIDRI

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关键词 川续断科; 裂叶翼首花; 三萜; 环烯醚萜甙

Key words Dipsacaceae; *Pterocephalus bretschnidri*; Triterpenoids; Iridoidal glycosides